

PATENT SPECIFICATION (11) 1 425 228

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(21) Application No. 6721/73 (22) Filed 12 Feb. 1973
 (23) Complete Specification filed 6 Feb. 1974
 (44) Complete Specification published 18 Feb. 1976
 (51) INT CL² C08K 5/05 A61K 7/11 C08K 5/02
 (52) Index at Acceptance
 C3P 12DX E2 PC14A PC14B PC16A PC16C PC20B
 ASB 774

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(54) HAIR SPRAYS AND SETTING LOTIONS

(71) We, THE GILLETTE COMPANY, a corporation organised under the laws of the state of Delaware, United States of America, of Prudential Tower Building, Boston, Massachusetts 02199, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention is concerned with hair sprays and setting lotions and with a particular mode of use of such setting lotions.

As is well known, hair sprays and setting lotions comprise a solution of a polymeric material in a solvent. When hair is contacted with the solution and the solvent then evaporated, a thin coating of the polymer is formed on the individual hairs and/or at cross-over points between two or more individual hairs (the former effect predominating when setting lotions are used in the conventional way and the latter when hair sprays are used), which polymer coating constrains the hairs in a desired configuration. There are three main criteria which determine the suitability or otherwise of a polymeric material as a hair spray or setting lotion ingredient.

10 Firstly, it must be soluble in suitable solvents. The usual solvent used in hair sprays is (for medical and other reasons) ethanol, although, in some countries, methylene dichloride and isopropanol are also used; the usual concentration of polymer in solution is about 2 to 4% by weight. Some setting lotions are aqueous and some comprise solutions in ethanol or aqueous ethanol; the usual concentration of polymer in solution is 3 to 5%.

15 Secondly, the polymer coating (on the hair) must not be water-sensitive, that is to say it must not become tacky when exposed to a humid atmosphere. In aqueous setting lotions, the polymers (being soluble in water) are generally more water-sensitive than polymers which are insoluble in water, but soluble in, say, alcohol.

20 Thirdly, the polymer coating (on the hair) must exhibit good "feel", that is it must be neither too brittle or stiff nor too soft and elastic.

25 It has been found in the past that whilst many homopolymers exhibit good "feel", none of these satisfactorily combines good solubility in ethanol with good resistance to humidity. In an attempt to overcome this problem, random copolymers have been used but, in general, these still have the disadvantage that either they are only poorly soluble in ethanol or they are water-sensitive.

30 We have now found that certain water-insoluble block copolymers are particularly useful in hair sprays and setting lotions in that they have both good solubility in organic solvents such as ethanol and, at the same time, good resistance to humidity. They also possess good "feel".

35 According to the present invention, we provide a hair spray or setting lotion, which comprises a 2 to 5% by weight solution in an organic solvent which is physiologically acceptable for application to hair on the head, of a water-insoluble block copolymer of the A-B-A type in which the segment B is a polymer having a glass transition temperature below normal room temperature and the segments A are a polymer having a glass transition temperature of 40°C or higher, the natures and relative proportions of the segments A and B being such that the block copolymer has adequate solubility in the organic solvent to provide a solution having a concentration within the said range.

40 Organic solvents which are physiologically acceptable for application to hair on the head include, as indicated above, ethanol, methylene chloride and isopropanol, though the latter two of these are not permitted for this purpose in some countries.

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As is well known, hair sprays are normally sold in aerosol formulations and the present invention includes within its scope aerosol hair spray formulations comprising a block copolymer solution according to the invention. In the case of setting lotions, the block copolymer solution may, if desired, contain water in an amount insufficient to cause precipitation of the block copolymer.

5 Polymers which have a glass transition temperature below room temperature are rubbery at room temperature, whilst those which have a glass transition temperature of 40°C or above are in a glassy state at room temperature. There are many suitable polymers for segments A and B, examples being polymers of:

10 A.
2-vinyl pyridine,
4-vinyl pyridine,
2-methyl-5-vinyl pyridine,
and

15 acrylamides and methacrylamides of the formula $\text{CH}_2=\text{C}(\text{R})\text{CONR}'\text{R}^2$, where R is H or CH_3 , R' is H or an *n*-alkyl group containing 3 or more carbon atoms, and R^2 is an *n*-alkyl group containing 3 or more carbon atoms.

B.
20 butadiene,
isoprene,
isobutene,
alkyl acrylates where the alkyl group contains from 2 to 12 carbon atoms,
alkyl methacrylates where the alkyl group contains from 4 to 12 carbon atoms,
vinyl *n*-alkyl ethers,
25 alkyl-substituted butadienes, and
chloroprene.

Whilst the present invention is primarily concerned with the use of block copolymers of the A-B-A type, the same advantageous combination of properties is also found in block copolymers containing additional B and A segments, that is, in generalised form, block copolymers of the A-B-(A-B)_n-A type, where n is an integer from 1 to 5, preferably 1 or 2, and segments A and B are as defined above. Such block copolymers are more complicated to prepare than A-B-A block copolymers and a multi-stage process is necessary; they are, therefore, more expensive to produce than A-B-A block copolymers and since they do not exhibit any significant improvement over the corresponding A-B-A copolymers, they are less preferred than the latter.

In these block copolymers, the segment B polymer will be insoluble in ethanol, whilst the segment A polymer will be soluble, so that when ethanol is used as the organic solvent of the hair spray or setting lotion, the proportion of A in the copolymer will be chosen so that the copolymer is soluble to the desired extent. The appropriate amount of A required to give the copolymer the desired solubility can be determined by routine trial and experiment. In the particular case where A is poly (2-vinyl pyridine) and B is polybutadiene, at least about 70% by weight of the copolymer should be poly (2-vinyl pyridine) if the copolymer is to be soluble in ethanol to form a 2%-4% solution.

It will be appreciated, however, that where other and better solvents, such as methylene dichloride or isopropanol, are used as the organic solvent in the hair spray or setting lotion, the segment B polymer itself may dissolve or nearly dissolve in the solvent and no, or very little, segment A polymer will be required to achieve the desired solubility. In such cases, preferred proportions of A and B in the copolymer will be determined by the "feel" and the water-sensitivity of the polymer.

50 The "feel" of the block copolymers will vary with the relative weight proportions of the segments A and B. Thus, where there is very little A, the copolymer will be rubbery and elastic, and where there is very little B, it will be harder and stiffer. The most desirable "feel" lies between these two extremes, but it is not necessarily achieved with 50/50 proportions of A and B. The precise proportions of A and B required to give the optimum "feel" will vary with the 55 nature of A and B and can be determined in any particular case by routine trial and experiment. When A is poly (2-vinyl pyridine) and B is polybutadiene, good "feel" can be obtained with polybutadiene contents varying from over 80% down to 10%.

The water-sensitivity of the copolymers will also vary depending on the proportions of A and B. Again, the optimum proportions, or range of proportions, can be determined by routine trial and experiment. In the case when A is poly (2-vinyl pyridine) and B is polybutadiene, good resistance to humidity is obtained when the amount of polybutadiene is 10% or greater.

60 It will be appreciated from the above that when a block copolymer in which A is poly (2-vinyl pyridine) and B is polybutadiene is to be used in a hair spray or setting lotion, as a 65 solution in ethanol, the optimum amount of segments A in the copolymer is from about 70% to

about 90%. In such cases, the copolymer has the desired solubility and good "feel". In addition, its resistance to humid conditions is very good and is substantially better than many of the random copolymers currently in use in hair sprays. Whilst the resistance to high humidity is very good, the polymers can still easily be removed from hair by shampooing. This excellent 5 resistance to humidity is achieved with amounts of segments A down to 20% or below, so that where the copolymer is to be used in solution in, say, methylene dichloride, the proportion of segments A can vary from 20% (or possibly less) up to over 80% for optimum properties.

As will be well understood, the viscosity and, to some extent, the solubility of the copolymers will vary with their molecular weight. In this connection, we have found it desirable (at 10 least where the polymers are to be used in aerosol hair sprays) to keep the molecular weight of poly (2-vinyl pyridine)/polybutadiene copolymers below about 100,000 since at higher levels, the polymer solution has a viscosity such that it tends to "jet" out of the aerosol dispenser rather than form a spray of fine droplets. It is also generally desirable to avoid high molecular weights because solubility tends to decrease with increasing molecular weight. As in the cases of 15 water-sensitivity, "feel" and solubility, routine trial and experiment will reveal the best 15 molecular weight ranges in any particular case.

In addition to using the setting lotions according to the invention in conventional ways, we have found that when the block copolymers present therein are of a particular kind, they can be used to obtain a semi-permanent set, that is a set which remains until the hair is next washed. 20 Such a semi-permanent set is obtained by applying the setting lotion to damp hair, combing the hair and setting it into the desired style, and then rapidly drying the hair at a temperature of 80° to 90°C for 2 to 3 minutes. Although this temperature of 80° to 90°C is considerably higher than is conventionally used in home or professional hair waving, it has been found that such 25 temperatures can be tolerated for the short drying periods required.

The set obtained in this way is substantially unaffected by conditions of high humidity because 30 of the good humidity resistance of the block copolymers according to the invention, but since it is dependent on the polymer coating on the individual hairs and on hair cross-over points and the polymer is removed by conventional shampooing, it is destroyed by washing the hair. After the hair has been washed, a further semi-permanent set may, of course, be applied in the 35 manner described.

In order to obtain this effect, it is necessary that the segments A of the copolymer should be of a polymer that has a glass transition temperature of from 50 to 90°C, the segment B being as defined above. The specific segment A polymers mentioned above, that is poly (2-vinyl pyridine), poly (4-vinyl pyridine), etc., all have glass transition temperatures above 90°C, but we have 40 found that these polymers are effectively plasticised by the perfuming agents conventionally incorporated in setting lotions to the extent that their glass transition temperatures are reduced to 90°C or less and lie in the range 40° to 90°C. The amount of such perfuming agents required to effect this reduction in the glass transition temperature is, in general, the amount in which they are normally present in setting lotions, that is from about 0.1 to 0.3% by weight of the setting 45 lotion, which is less than 10% by weight of the normal polymer content of setting lotions. Plasticisers which reduce the glass transition temperature of such polymers to within the range 40° to 90°C and which are not perfuming agents can, of course, also be used, but since toiletries such as setting lotions almost invariably contain perfuming agents, it is convenient not to use an added non-perfuming plasticiser and to use only one or more perfuming agents which have a 50 plasticising effect.

Whilst the block copolymers with which this invention is concerned can be made, at least on a laboratory scale, in several ways, we believe that the best method currently available (and which could be operated on a commercial scale) is the so-called "living polymer" method. This is a well-known technique for preparing block copolymers and no detailed description will, 55 therefore, be given. Essentially, the method comprises first forming the middle segment B by polymerising the appropriate monomer, and then forming simultaneously on to the two ends of segment B, the segments A by polymerising the appropriate monomer in the presence of the already formed segment B. The polymerisation is initiated in the presence of a solvated electron solution, such as is formed by mixing sodium and naphthalene in tetrahydrofuran or by lithium butyl. To make copolymers containing additional B and A segments, the procedure is 60 repeated, first to form one or two additional B segments and then to form one or two additional A segments, and further repeated as required.

As is well known, block copolymers prepared by the "living polymer" method have a very narrow molecular weight distribution and this is an advantage in preparing the copolymers with 65 which we are concerned.

It will also be appreciated that not all monomers can be polymerised by this method. For example, monomers containing a carboxyl group cannot be polymerised by the "living polymer" method and, in such cases, another procedure must be used.

The block copolymers used according to the invention can be characterised by any of the 65 parameters normally applied to polymers. The fact that they are block copolymers is normally

established by the method of preparation used, the method not being capable of giving rise to a random copolymer or a graft copolymer; this is, in particular, the case when the "living polymer" method is used.

The relative proportions of A and B segments in the block copolymer can be determined by a number of methods. Thus when one of the segments contains an atom, such as nitrogen or chloride, which is not present in the other, the block copolymer can be analysed to determine the percentage of such atom present and by computation from the percentage of such atom in a homopolymer of that segment, the proportion of that segment in the block copolymer can be determined. In addition to elemental analysis, the absorbance of a solution of the block copolymer in a suitable solvent at a particular wavelength in the ultra-violet region characteristic of an atom present in one segment, but not in the other, may be used.

For example, in the case of block copolymers in which the A segments are derived from 2-vinyl pyridine, 4-vinyl pyridine or an acrylamide or methacrylamide of the formula $\text{CH}_2=\text{C}(\text{R})\text{CONR}^1\text{R}^2$ and the B segment is derived from butadiene or any of the other specific B monomers referred to above, nitrogen estimation may be carried out by the Dumas method or the U.V. absorbance of a solution of the block copolymer at $263\text{ m}\mu$ may be measured.

A further method of determining the relative proportions of the A and B segments in the block copolymers is by infra-red analysis, the size of a first peak in the I.R. spectrum characteristic of the A monomer being compared with the size of a second peak characteristic of the B monomer. By such comparison, a quantitative determination of the relative proportions of the two segments can be made. By way of example, for the block copolymer in which the A segments are derived from 2-vinyl pyridine and B segment from butadiene, the peaks at 9.55μ and 6.1μ , respectively, are measured.

When the block copolymer is produced by the "living polymer" method care is taken to polymerise all of the B segment monomer introduced before introducing any of the A segment monomer and then to ensure that all of the A segment monomer introduced is polymerised, it is found that the relative proportions of A and B segments in the final copolymer are substantially identical with the relative proportions of the monomers used.

In order that the invention may be more fully understood, the following examples are given by way of illustration only:—

EXAMPLES 1-6

Six block copolymers of the A-B-A type were made by the "living polymer" method, in which A was poly (2-vinyl pyridine) and B was polybutadiene, the copolymers differing in the relative proportions of A segments and B segment they contained.

The procedure used for making the first of the copolymers was as follows:

All solvents and reactants used were vigorously dried and the reaction was carried out in vacuum or under absolutely dry argon that was free of oxygen.

51.2 mls of the initiator solution, a 0.166 molar solution of sodium naphthalene in tetrahydrofuran, were introduced into a reaction vessel under vacuum. The vessel was cooled to -110°C and 38.8 grams of 1,3-butadiene were distilled in. The mixture was allowed to warm up to 0°C as dry argon was introduced into the vessel. A solution of "living" polybutadiene in tetrahydrofuran was obtained which had a bright orange colour. When the butadiene polymerisation was complete, the vessel was once again cooled down to -100°C and 161.2 grams of 2-vinyl pyridine were introduced while the mixture was stirred at high speed. The colour of the solution changed from the orange of the butadiene to the cherry red colour of poly (2-vinyl pyridine). The solution was allowed to warm up to room temperature and then allowed to stand for one hour. The "living" polymer was then terminated by the addition of methanol to the mixture and a colourless copolymer solution was obtained. The copolymer was isolated by precipitation with ether.

Alternatively, the copolymer could be isolated by spray drying the final reaction mixture.

The intrinsic viscosity of the copolymer was determined in solution in methanol at 30°C and was found to be 0.33.

The relative proportions of A and B segments in the copolymer were determined by nitrogen analysis and from the infra-red spectrum at 6.1μ (for butadiene) and 9.55μ (for vinyl pyridine) as described above, and were found to be the same as the relative proportions of the monomers used, that is 80.6% of A segments and 19.4% of B segment.

Five other block copolymers having the same A and B segments, but in different proportions, were made in the same way by appropriate adjustment of the amounts of the two monomers used. The relative proportions of A and B segments in these block copolymers and the intrinsic viscosities of two of the polymers are given in Table I below (these intrinsic viscosities were measured in toluene).

All six copolymers were soluble in methylene chloride, but only copolymers 1 and 2 were soluble (to form a 3% solution) in ethanol.

The set holding properties of the polymers were determined by a roller frame method. This consisted of testing 1 gram tresses of hair curled in an undulating wave pattern on 1.8 cm

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diameter rollers. Each end of the tress was glued to a small card weighing 0.5 gram, the cards being 14.5 cms apart. The tresses were thoroughly wetted under running water, lightly combed and set in the roller frame and allowed to come to equilibrium at 30% relative humidity (R.H.) overnight.

5 The copolymers to be tested were dissolved in methylene chloride to form 3% solutions. After the overnight equilibration, the tress on the roller frame was dipped into one of the 10 3% solutions, excess solution was shaken off, and the tress was allowed to dry for one hour at 30% R.H. and 25°C; the amount of polymer deposited on the hair (the "add-on") was about 80 mg/gram of hair. The tress was then removed from the roller frame and the distance 15 between the two cards was measured while the tress hung vertically; at this stage, the tress was also examined for "feel". The tress was then placed in a cabinet at 90% R.H. and 24°C for 2 hours, after which time the tress was removed, hung vertically, and the distance between the cards was re-measured.

The hanging length for 100% relaxation of the set was 14.5 cms; the hanging length for zero 15 relaxation was 11.0 cms (this figure being a function of the size of the roller frame):

$$\% \text{ relaxation} = \frac{14.5 - 11.0}{14.5 - 11.0} \times 100.$$

$$\% \text{ retention} = 100 - \% \text{ relaxation}.$$

20 (It will be appreciated from this description, that the higher the "% retention" figure, the better the resistance to humidity of the polymer tested.)

In addition to testing the six block polymers in this way, 3% solutions in methylene chloride of the random copolymers X and Y which are currently used in commercially available 25 setting lotions and hair sprays, were also tested in the same way. Details of the block copolymers, and the test results obtained, are shown in Table I.

TABLE I

Ex./Polymer	A segments	B segment	Intrinsic viscosity	% retention
1.	80.6%	19.4%	0.33	88
	70.5%	29.5%	—	89
	60%	40%	—	91
	50%	50%	0.60	94
	40%	60%	0.76	94
	25%	75%	—	80
X	—	—		60
Y	—	—	63-74	40

The tresses set with solutions of copolymers 1 to 6 all had good "feel". As can be seen from the table, all of the copolymers 1 to 6 had substantially better resistance to humidity than did X and Y.

45 The intrinsic viscosity figures given in the table indicate that all of copolymers 1 to 6 had a molecular weight of about 100,000.

EXAMPLES 7 and 8

50 Two block copolymers of the A-B-A type in which the A segments were poly (2-vinyl pyridine) and the B segment was polybutadiene, were prepared as described for Examples 1 to 6. The relative proportions of the A and B segments in the copolymers were determined as described for Examples 1 to 6 and were found to be the same as the relative proportions of the monomers used.

55 These two copolymers were tested as hair spray polymers. For this purpose they were used in the form of 2% solutions in ethanol. The set retention test used was as described for Examples 1 to 6, the tress, after the overnight equilibration on the roller frame, being sprayed with the polymer solution by means of a De Vilbis type EGA-502 air gun held at a distance of 20 cms. Spraying was carried out so that the amount of polymer deposited on the hair from the tress. Spraying was carried out so that the amount of polymer deposited on the hair (the "add-on") was 6 to 10 mg/gram of hair. Drying of the tress, the exposure to conditions of high humidity, and the two measurements of tress length were carried out as described for Examples 1 to 6.

In addition to testing the two block copolymers, two commercially available hair sprays X and Y were also tested in the same way.

65 Details of the block copolymers and the results of testing are shown in Table II.

TABLE II

Ex./Polymer	A segments	B segment	% retention	
5				5
7.	80.0%	20%	71	
8.	90.0%	10%	79	
X	-	-	25	
Y	-	-	50	
10				10
	Block copolymers 7 and 8 gave an excellent "feel". It will be seen from the table that these two polymers had better humidity resistance than the polymers of the commercially available hair sprays.			
		EXAMPLE 9		
15	A block copolymer of the A-B-A type comprising 50% A segments of poly (4-vinyl pyridine) and 50% B segment of poly (2-ethylhexyl methacrylate) was prepared as described for Examples 1 to 6, but using 100 grams of 2-ethylhexyl methacrylate in place of the 1,3-butadiene and 100 grams of 4-vinyl pyridine in place of the 2-vinyl pyridine.		15	
20	The relative proportions of A and B segments were determined as described for Examples 1 to 6.		20	
25	The set retention of this copolymer when used as a setting lotion and tested as described in Examples 1 to 6, was 83%.		25	
	EXAMPLE 10			
30	A block copolymer of the A-B-A type comprising 50% A segments of poly (4-vinyl pyridine) and 50% B segment of poly (<i>n</i> -butyl methacrylate) was prepared as described for Examples 1 to 6, but using 100 grams of <i>n</i> -butyl methacrylate in place of the 1,3-butadiene and 100 grams of 4-vinyl pyridine in place of the 2-vinyl pyridine.		30	
35	The relative proportions of A and B segments were determined as described in Examples 1 to 6.		35	
40	The set retention of this copolymer when used as a setting lotion and tested as described in Examples 1 to 6, was 81%.		40	
	WHAT WE CLAIM IS:—			
45	1. A hair spray or setting lotion, which comprises a 2 to 5% by weight solution in an organic solvent which is physiologically acceptable for application to hair on the head, of a water-insoluble block copolymer of the A-B-A type in which the segment B is a polymer having a glass transition temperature below normal room temperature and the segments A are a polymer having a glass transition temperature of 40°C or higher, the natures and relative proportions of the segments A and B being such that the block copolymer has adequate solubility in the organic solvent to provide a solution having a concentration within the said range.		45	
50	2. A hair spray or setting lotion according to claim 1, in which the segments A are a polymer of 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, or an acrylamide or methacrylamide of the formula $\text{CH}_2=\text{C}(\text{R})\text{CONR}'\text{R}^2$, where R is H or CH_3 , R' is H or an <i>n</i> -alkyl group containing 3 or more carbon atoms, and R^2 is an <i>n</i> -alkyl group containing 3 or more carbon atoms.		50	
55	3. A hair spray or setting lotion according to claim 1 or 2, in which the segment B is a polymer of butadiene, isoprene, isobutene, an alkyl acrylate where the alkyl group contains from 2 to 12 carbon atoms, an alkyl methacrylate where the alkyl group contains from 4 to 12 carbon atoms, a vinyl <i>n</i> -alkyl ether, an alkyl-substituted butadiene, or chloroprene.		55	
60	4. A hair spray or setting solution according to any of claims 1 to 3, in which the organic solvent is ethanol, methylene chloride, or isopropanol.		60	
65	5. A hair spray or setting lotion according to any of claims 1 to 4, in which the segments A are poly (2-vinyl pyridine) and the segment B is polybutadiene.		65	
	6. A hair spray or setting lotion according to claim 5, in which the block copolymer has a molecular weight of less than 100,000.			
	7. A hair spray or setting lotion according to claim 5 or 6, in which the organic solvent is ethanol and the block copolymer contains from 70 to 90% by weight of segments A and, complementally, from 30 to 10% by weight of segment B.			
	8. A hair spray or setting lotion according to claim 5 or 6, in which the organic solvent is methylene chloride and the block copolymer contains from 20 to 80% by weight of segments A and, complementally, from 80 to 20% by weight of segment B.			
	9. An aerosol hair spray, which comprises a block copolymer solution according to any of claims 1 to 8 as part of an aerosol formulation.			
	10. A setting lotion according to any of claims 1 to 8, which additionally comprises water in an amount insufficient to cause precipitation of the block copolymer.			

11. A hair spray or setting lotion, which comprises a 2 to 5% by weight solution in an organic solvent which is physiologically acceptable for application to hair on the head, of a water-insoluble block copolymer of the A-B-(A-B)_n-A type, where n is an integer from 1 to 5 and segments A and B are as defined in claim 1, the natures and relative proportions of the segments A and B being such that the block copolymer has adequate solubility in the organic solvent to provide a solution having a concentration within the said range. 5

12. A hair spray or setting lotion according to claim 11, in which n is 1 or 2.

13. A hair spray or setting lotion according to claim 11 or 12, in which the segments A are as specified in claim 2.

10 14. A hair spray or setting lotion according to any of claims 11 to 13, in which the segments B are as specified in claim 3.

15 15. A hair spray or setting lotion according to any of claims 11 to 14, in which the segments A are poly (2-vinyl pyridine) and the segments B are polybutadiene.

16. A method of imparting a semi-permanent set to hair, which comprises applying 15 to damp hair, a setting lotion which comprises a 2 to 5% by weight solution in an organic solvent which is physiologically acceptable for application to hair on the head, of a water-insoluble block copolymer of the A-B-(A-B)_n-A type, where n is 0 or an integer from 1 to 5, each B segment is a polymer having a glass transition temperature below normal room temperature and each A segment is a polymer having a glass transition temperature of from 20 50° to 90°C, the natures and relative proportions of the segments A and B being such that the block copolymer has adequate solubility in the organic solvent to provide a solution having a concentration within the said range, combing the hair and setting it into the desired style, and then rapidly drying the hair at a temperature of 80° to 90°C for 2 to 3 minutes.

17. A method of imparting a semi-permanent set to hair, which comprises applying 20 to damp hair, a setting lotion which comprises a 2 to 5% by weight solution in an organic solvent which is physiologically acceptable for application to hair on the head, of a water-insoluble block copolymer of the A-B-A type, in which the segment B is a polymer having a glass transition temperature below normal room temperature and the segments A are of a polymer having a glass transition temperature above 90°C, the natures and relative proportions 25 of the segments A and B being such that the block copolymer has adequate solubility in the organic solvent to provide a solution having a concentration within the said range, the setting lotion also containing a quantity of a plasticiser for the A segments which is sufficient to reduce the glass transition temperature thereof to a value in the range 50° to 90°C, combing the hair and setting it into the desired style, and then rapidly drying the hair at a temperature 30 of 80° to 90°C for 2 to 3 minutes.

18. A method according to claim 17 in which the A segments are as specified in claim 2.

19. A method according to claim 17 or 18, in which the B segment is as specified in claim 3.

20. A method according to any of claims 17 to 19, in which the plasticiser is a perfuming agent. 35

40 21. A method according to claim 20, in which the setting lotion contains from 0.1 to 0.3% of plasticiser, based on the weight of the setting lotion.

22. A setting lotion comprising any one of Polymers 1 to 6 substantially as herein described in any of Examples 1 to 6.

23. A hair spray comprising Polymer 7 or 8 substantially as herein described in Example 40 45 7 or 8.

24. A setting lotion comprising a polymer substantially as herein described in either Example 9 or 10.

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